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MODEL FOR KINETICS OF HYDROGEN-INDUCED DIRECT PHASE TRANSFORMATIONS IN R_2Fe_{17} (R – Sm, Y) TYPE ALLOYS

Model for evolution of the hydrogen induced direct phase transformation in R_2Fe_{17} (R – Sm, Y) type hard magnetic alloys has been proposed. It is shown that evolution process of hydrogen-induced direct phase transformation in R_2Fe_{17} type hard magnetic alloys is controlled by diffusion process of Fe atoms in low temperatures interval of 330–750 °C and in high temperatures interval of 780–860 °C phase transformation process is controlled by growth kinetics of rare-earth RH_2 hydride phase. In accordance with above described model on the base of Kolmogorov and Lyubov kinetic theory of the phase transformations has been obtained kinetic equation that well described the isothermal kinetic diagram for this type transformation in R_2Fe_{17} (R – Sm, Y) type hard magnetic alloys.

Keywords: kinetics, phase transitions, magnetic alloys.

МОДЕЛЬ КИНЕТИКИ ИНДУЦИРОВАННЫХ ВОДОРОДОМ ПРЯМЫХ ФАЗОВЫХ ПРЕВРАЩЕНИЙ В СПЛАВАХ ТИПА R2FE17 (R – SM, Y)

Предложена модель для развития индуцированного водородом прямого фазового превращения в магнитотвердых сплавах типа R_2Fe_{17} (R – Sm, Y). Показано что процесс развития индуцированного водородом прямого фазового превращения в магнитотвердых сплавах типа R_2Fe_{17} контролируется процессами диффузии атомов Fe в низкотемпературном интервале 330–750 °C и в высокотемпературном интервале 780–860 °C процесс превращения контролируется кинетикой роста гидридной фазы RH_2. В соответствии с вышеописанной моделью на основе кинетической теории фазовых превращений Колмогорова и Любова получено кинетическое уравнение, хорошо описывающее изотермическую кинетическую диаграмму для превращений такого типа в магнитотвердых сплавах типа R_2Fe_{17} (R – Sm, Y).

Ключевые слова: кинетика, фазовые переходы, магнитные сплавы.

At present the intermetallic compounds of R_2M_{17} (R = Sm, Y, Dy, Ho, Gd) type have attracted much attention because of their interesting magnetic properties. For instance, R_2M_{17} compounds demonstrate very interesting

magnetic phenomenon during their interaction with interstitial atoms (H, N, C, B).

In particular, the new perspective technology well known as a HDDR-process (Hydrogenation-Decomposition-Desorption-Recombination) in R_2M_{17} type alloys (Sm_2Fe_{17}, Sm_2Co_{17} etc.) alloys for permanent magnets allows improve their structure and magnetic properties by hydrogen-induced reversible phase transformations. It is obvious that a clear understanding of the kinetic peculiarities of hydrogen-induced phase transformations will allow control of the microstructure and magnetic properties of these materials too.

The isothermal kinetic diagrams of the hydrogen induced direct phase transformations in Sm_2Fe_{17} and Y_2Fe_{17} alloys were obtained experimentally earlier [1; 2]. However, to the present moment some kinetic equation describing isothermal kinetic diagram above-mentioned phase transformations doesn't exist. Thus, the main goal of the present paper is to describe above mentioned isothermal kinetic diagram theoretically within the framework of classical kinetic theory of phase transformation in condensed state.

At first stage, at HDDR-treatment the R_2Fe_{17} alloy undergoes the direct hydrogen-induced phase transformation at temperatures above 500 °C in hydrogen atmosphere about 0.1 MPa with decomposition of initial alloy on hydride YH_2 phase and α-phase of Fe that can be described by the following phase scheme:

$$R2Fe17 + H2 \rightarrow RH2 + \alpha\text{-}Fe \qquad (1)$$

Then, the reverse phase transformation takes place during hydrogen evacuation at higher temperatures with recombination decomposed phases into initial Y_2Fe_{17} matrix phase and can be described by the following phase reaction:

$$RH2 + \alpha\text{-}Fe \rightarrow R2Fe17 + 2H2\uparrow \rightarrow R2Fe17 \qquad (2)$$

Earlier on a base of detailed kinetic investigations, SEM and X-ray diffraction studies during direct phase transformation (see Eq. (1)) in $Nd_2Fe_{14}B$, Sm_2Fe_{17} and Y_2Fe_{17} type alloys it was established that transformations of this type maybe classified as diffusive phase transformation in solid state and that the direct transformation process proceeds by the nucleation and growth mechanism [1; 2].

As follows from Becker-Döering model of nucleation kinetics if plots dependence $\ln t_\xi$ on $1/T$, where t_ξ is the time, which is needed for reaching of some degree of transformation ξ and T is the temperature, we can determine an effective energy of phase transformation process. For this goal experimental data were re-plotted in co-ordinates $\ln t_\xi$ versus $1/T$. The slopes of the straight

lines give us the values of the effective activation energies for hydrogen induced direct phase transformations. The obtained values of an activation energy determined for some degrees of transformation varying from 109 up to 230 kJ/mol for Sm_2Fe_{17} alloy [1] and from 162 up to 242 kJ/mol for Y_2Fe_{17} alloy [2]. Obtained above values of effective activation energy in low temperature region (330–750 °C) have good agreement with an activation energy of data for diffusion of Fe atoms in Rare-Earth metals – Q = 250 kJ/mol [1; 2] and self-diffusion of Fe atoms in α-Fe phase of iron ~250.6 kJ/mol. For comparison activation energy for hydrogen atoms diffusion in R_2Fe_{17} type alloys equals ~(31±10) kJ/mol that less by one order of values. Earlier it was established that for $Nd_2Fe_{14}B$ alloy in high temperature region (780–860 °C) effective energy activation is equal to the energy of NdH_2 hydride phase formation (ΔG_{NdH2}= – (187.7±3.3) kJ/mol). Therefore, it is really possible to consider that evolution process of direct phase transformation is controlled by diffusion process of Fe atoms in low temperatures interval of 330–750 °C and in high temperatures interval of 780–860 °C phase transformation process controlled by growth kinetics of rare-earth RH_2 hydride phase. On the other hand, as can be seen from scheme (1) there is a reason to believe that diffusion of hydrogen into R_2Fe_{17} alloy leads to nucleation and growth process of RH_2 hydride phase and then diffusion of Fe atoms leads to formation of α-Fe phase.

Thus, in our case we can believe that evolution process of transformation is controlled by two main process, i.e. nucleation and growth process of the two main phases: RH_2 hydride phase and α-Fe phase. In accordance with above described model let's obtain kinetic equations for direct hydrogen induced phase transformation in R_2Fe_{17} type alloys. As well known from the Kolmogorov kinetic theory of phase transformation in solid state [3], the volume of the transformed area ξ in dependence on t transformation time can be written as

$$\xi(t) = \frac{V(t)}{V_o} = 1 - \exp\left[-\int_0^t I(t)\varphi(t-\tau)dt \right], \tag{3}$$

where $V(t)$ is the transformed area volume at time t, V_o is the initial volume, $I(t)$ is the nucleation rate of centres of new phases at time t, $\varphi(t)$ is the volume of this nucleation centre at time t, τ is the nucleation moment of centre of a new phase. For the isothermal conditions as in our case it is believed that $I(t) = I$ = const.

In general case, according to the Lyubov kinetic theory approach [3] integral in Eq. (3) we can divide in two integrals: from 0 to τ and from τ to t, where τ is time which is necessary for growth of nucleus of new phase up to critical size. Thus, equation (3) maybe written in following form:

$$\xi(t) = 1 - \exp\left[-\left(\int_0^{\tau} I\varphi_1(t-\tau)dt + \int_{\tau}^{t} I\varphi_2(t-\tau)dt \right) \right], \tag{4}$$

where τ is time which is necessary for growth of nucleus of new phase up to critical size, $\varphi_1(t)$ and $\varphi_2(t)$ is the volume of new phases of RH_2 and α-Fe nucleation centres at time moment *t*, correspondingly.

Further, growth of volume of a spherical centre of RH_2 phase $\varphi_1(t)$ may be written as:

$$\varphi_1(t) = \frac{4}{3}\pi r_1^3(t), \tag{5}$$

where $r_1(t)$ is the radius of this centre at time *t*.

Nucleation process of RH_2 phase we can be considered as in single-component system taking into account of high diffusive mobility of hydrogen atoms to rare-earth atoms in R_2Fe_{17} alloy and in this case according to theory of absolute reaction rates [3] radius $r_1(t)$ of RH_2 centre at time *t*:

$$r_1(t) = \frac{\pi d^4 \Delta g}{9h} e^{-\frac{U}{RT}} t, \tag{6}$$

where Δg is change of free energy at formation of volume unit of new phase, *U* is activation energy of atoms at transition through interface of phases, *d* is diameter of diffusing atom (hydrogen atoms in our case), *h* is the Planck constant, *R* is the gas constant, *T* is transformation temperature, *t* is some time moment.

Analogously, growth of volume of a spherical centre of α-Fe phase $\varphi_2(t)$ may be written as:

$$\varphi_2(t) = \frac{4}{3}\pi r_2^3(t), \tag{7}$$

where $r_2(t)$ is the radius of α-Fe centre at time *t*.

On the other hand, it's known [3] that at diffusive-controlled transformations boundary of new phase moves by parabolic low and $r_2(t)$ may be written in following form:

$$r_2(t) = 2\beta\sqrt{D\,t}, \tag{8}$$

where $D = D_o e^{-\frac{Q}{RT}}$ is the diffusion coefficient of Fe atoms, *Q* is the activation energy of Fe atoms diffusion, *R* is the gas constant, β is kinetic parameter, *T* is the transformation temperature, *t* is some time moment.

Further, rate of nucleation *I* of new phase's centers in condensed systems in accordance with Turnbull-Fisher model [3] is

$$I = \gamma \frac{RT}{h} e^{-\frac{W}{RT}} e^{-\frac{U}{RT}}, \tag{9}$$

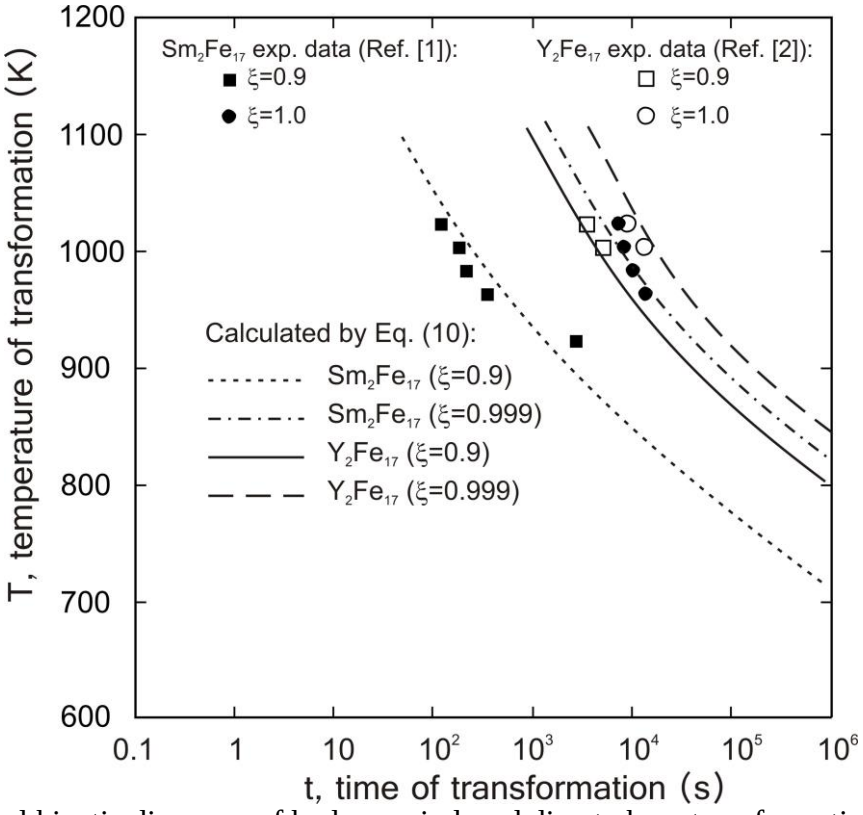
where *W* is the energy necessary for formation of critical nucleus, *U* is the activation energy at transition of atoms through interface of phases, $\gamma = 10^6$ mol/m^3, *R* is the gas constant.

Then, substitute equations (4)–(9) in (3) we can obtain kinetic equation for volume of the transformed area ξ in dependence on *t* transformation time and

temperature T, and then for time dependence for direct hydrogen-induced phase transformations in R_2Fe_{17} type alloys from ξ and T in low temperature region (330–750 °C) we can obtain the following equation:

$$t(\xi,T)=\left(\frac{15h}{64\pi\gamma R\beta^3(\xi)D_o^{\frac{3}{2}}}\right)^{\frac{2}{5}}\cdot\left[-\ln(1-\xi)\right]^{\frac{2}{5}}\left[\frac{1}{T}\right]^{\frac{2}{5}}\cdot e^{\frac{\frac{2}{5}(W+U)+\frac{3}{5}Q}{RT}}. \qquad (10)$$

Then on the base of Eq. (10) and data from [1; 2] the isothermal kinetic diagrams for direct hydrogen-induced phase transformation in low temperatures interval (330–750 °C) in R_2Fe_{17} (R – Sm, Y) type alloys have been plotted. These diagrams are shown in fig. As can be seen from this figure the calculated curves well approximate experimental kinetic data from papers [1; 2].



The isothermal kinetic diagrams of hydrogen induced direct phase transformation in R2Fe17 (R – Sm, Y) type alloys calculated by Eq. (10) for different degrees of transformation ζ

Finally, kinetic equation of form Eq. (10) obtained on the base of Kolmogorov and Lyubov kinetic theory of the phase transformations well describes the kinetics of hydrogen induced direct phase transformations in R_2Fe_{17} alloys. It is possible the above-mentioned kinetic approach in future can be applied for others RE-Fe type hard magnetic alloys for permanent magnets (Pr-Fe, Er-Fe, Ho-Fe etc.).

REFERENCES

1. The kinetics of hydrogen-induced diffusive phase transformations in Sm_2Fe_{17} alloys / V. A. Goltsov [et al/] // Int. J. Nuclear Hydrogen Production and Applications. 2009. V. 2. № 1. P. 42−54.
2. Dodonova E. V., Rybalka S. B. Kinetics of hydrogen-induced direct phase transformation in Y_2Fe_{17} hard magnetic alloy // Letters on Materials. 2013. V. 3. P. 209−211.
3. Lyubov B.Ya. The kinetic theory of phase transformations. M.: Metallurgiya, 1969. P. 263.